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Poly(vinyl alcohol) hydrogels

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Abstract. Poly(vinyl alcohol) was used as base material for hydrogel preparation. The water absorption, gel fraction, and density of different gels prepared by the freezing/thawing method were studied.

Key words: poly(vinyl alcohol), gels, water absorption, gel fraction.

INTRODUCTION

Poly(vinyl alcohol) (PVA) is a hydrophilic polymer which is of special interest for the application in medicine owing to its excellent biocompatibility. Poly(vinyl alcohol) is one of the most ancient polymers and at the same time the most popular one used in this field.

Wound dressings have great importance in the therapeutic system. They must absorb the exudates and at the same time guarantee temporary physiological covering and efficient protection of the wound from mechanical trauma, thereby providing the necessary conditions for successful healing (normal moisture level at the bed of the wound, prevention of necrotic tissue forming, etc.) [1].

For that reason PVA hydrogels are of particular interest for application in wound healing systems. These are harmless, sterile, biocompatible, transparent (allow easy control of the healing process), and above all able to absorb water efficiently.

Hydrogels can be obtained in various ways. The following methods are most widely employed: chemical cross-linking [2]; mostly using glutaraldehyde as the cross-linking agent [3]; cross-linking by γ radiation [4,5], by UV radiation [6], and by use of successive freezing/thawing cycles [7,8]. Intermolecular bonds (mostly hydrogen bonds), which form during the freezing/thawing process of PVA water solutions, act as efficient cross-links [9].

The aim of this paper is to ascertain the impact of PVA molecular weight on gel formation as well as on the water absorption and density of gels prepared by the freezing/thawing method.

MATERIALS AND METHODS
Base materials

Several types of partially crystalline PVA were used for investigation: PVA I – mol. weight 130 000, T_m 225.8 °C and T_g 76.6 °C (according to DSC – differential scanning calorimetry method); PVA II – mol. weight 145 000 with the degree of hydrolization ≥98% (supplied by *Merck Schuchardt*); PVA III – mol. weight 88 000; degree of hydrolization 88% (supplied by *Acros Organics*); and PVA IV – molar mass weight 25 000 (supplied by *Fisher Scientific*).

Preparation of gel systems

Poly(vinyl alcohol) distilled water solutions with a determined polymer content were poured out on glass vessels. Next the solutions were exposed to successive cycles of freezing (one to three) for 12 h at −20 °C and thawing at 25 °C (12 h) [2].

Gel fraction

Cross-linking does not occur entirely. Besides gel, certain portion of PVA macromolecules remains in the

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network uncross-linked (sol). The gel fraction G in hydrogels was estimated by the formula

$$G(\%) = \frac{W_1}{W_d} \times 100, \qquad (1)$$

where W_1 is the weight of the dried cross-linked sample with sol and W_d is the weight of the dried sample after the removing of sol by extraction in water.

Determination of the equilibrium water content

Water uptake (swelling) of gel samples was measured at temperature levels of 20, 25, 30, and 37 °C (the last level simulates water absorption at the temperature of the human body) in a thermostatically controlled chamber to the equilibrium state. Dry gel samples (dried at 25 °C) were immersed in distilled water. Swollen samples were removed and immediately weighed (after the superficial water was wiped off using absorbent paper).

The equilibrium water content in swollen samples W_{eq} was calculated as follows:

$$W_{eq}(\%) = \frac{W_s - W_d}{W_s} \times 100, \qquad (2)$$

where W_s is the weight of the swollen sample at equilibrium state and W_d is the weight of the dry sample [10].

Density of gels

The density of dry gels was determined by hydrostatical weighing by kit *YDK 01LP* in ethanol (EN 1183-1:2004).

The density of gels was calculated by the formula

$$\rho = \frac{W_a \cdot \rho_l}{W_a - W_{sl}}, \qquad (3)$$

where W_a is the weight of the sample in air, ρ_l is the density of the liquid (ethanol), and W_{sl} is the weight of the sample in the liquid.

Differential scanning calorimetry

The differential scanning calorimeter *Mettler DSC 30* was used. Dried samples were heated from 20 °C to 300 °C at the heating rate of 10 °C/min. The average crystallinity was calculated by comparing the heat required to melt the polymer with the heat required to melt a 100% crystalline PVA (138 J/g).

RESULTS AND DISCUSSION

Gel fraction

The high content of the separated sol fraction (>50 to 60%) was noticed for dilute polymer solutions (content of PVA 5 and 10 mass%). Therefore, for further experiments 15% PVA solutions were used.

Yield of gel strongly depends on the type of polymer and number of freezing/thawing cycles. Gel fraction values are presented in Table 1. Thus polymers with a low value of molecular weight either poorly form gel (PVA III) or do not form gel at all (PVA IV). The gel content of polymers with a higher molecular weight increases with the number of freezing/thawing cycles. Yet, satisfactory values of gel fraction could be reached even at the first freezing/thawing cycle.

Water absorption

Water absorption of dry gels turned out to be quite rapid. Values of water content close to the equilibrium value W_{eq} can be reached in 2–4 h of exposure (Fig. 1).

An increase in the absorption rate (Fig. 1) and the equilibrium value of water content W_{eq} (Fig. 2) with the rise of the exposure temperature was noticed. The main reason seems to be the increase in the compliance of the cross-linked network.

Table 1. Gel fraction (G) for various PVA as a function of the number of freezing/thawing cycles (molecular weight $\times 10^{-3}$ in brackets)

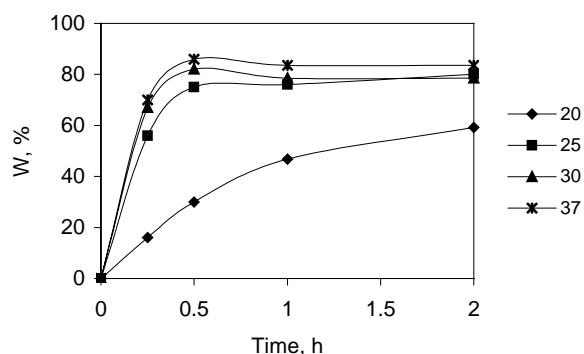| Number of cycles	G, wt%			
	PVA IV (25)	PVA III (88)	PVA I (130)	PVA II (145)
1	Does not form	–	68.8	82.4
2	gel	–	71.0	83.5
3		≈70	82.3	87.7

Fig. 1. Water absorption W as a function of the exposure time (initial 2 h) of PVA I gels obtained in the first freezing/thawing cycle (curves – temperature of exposure in °C).
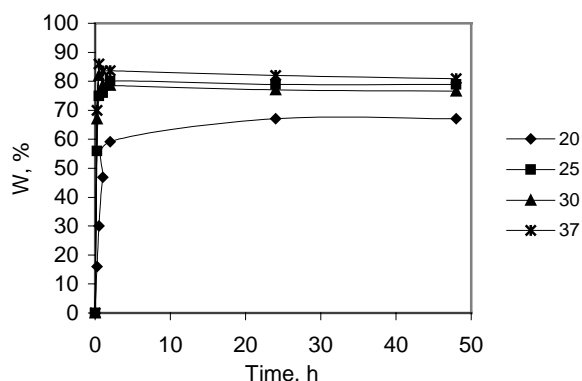
Fig. 2. Water absorption W as a function of the exposure time of PVA I gels obtained in the first freezing/thawing cycle (curves – temperature of exposure in °C).

Water absorption curves for elevated exposure temperature values show maxima, followed by a slight decrease in W values (2–3%) most probably due to loss of residues of the uncross-linked part of the polymer, which dissolves in water.

It was observed that the number of freezing/thawing cycles affects W_{eq} values negligibly (Fig. 3). The value $W_{eq} > 70\%$ can be obtained already in the first cycle.

It was of special interest to check the reversibility of water absorption of gels. Swollen samples were dried at room temperature and repeatedly immersed in distilled water. The equilibrium water content W_{eq}^* was determined.

Repeated water absorption shows that W_{eq}^* values do not differ significantly from the respective W_{eq} values. This indicates that the cross-linked network structure of the obtained gels is stable enough (Table 2).

It should be noted that W_{eq}^* values for PVA I are a bit higher than the respective W_{eq} values. This results from a slight decrease in the cross-linking degree of gels in the repeated swelling process (Table 2).
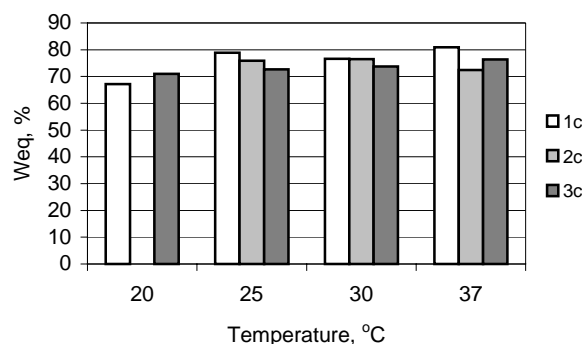

Fig. 3. Equilibrium values of water content (W_{eq}) for PVA I gels at different temperatures and the number of freezing/ thawing cycles (c).

Table 2. The equilibrium water content W_{eq} (first immersion) and W_{eq}^* (repeated immersion) as a function of the number of freezing/thawing cycles for polymers PVA I and PVA II at different exposure temperatures (ratio W_{eq}/W_{eq}^* in brackets)

Number of freezing/ thawing cycles	PVA I		PVA II	
	First immersion (W_{eq})	Repeated immersion (W_{eq}^*)	First immersion (W_{eq})	Repeated immersion (W_{eq}^*)
30 °C				
1	76.6	80.3 (1.05)	–	–
2	76.5	80.5 (1.05)	76.5	76.7 (~1)
3	73.8	77.6 (1.05)	74.2	76.4 (1.03)
37 °C				
1	80.9	87.2 (1.08)	78.0	77.8 (~1)
2	72.5	84.0 (1.16)	77.5	76.6 (~1)
3	76.4	81.0 (1.06)	77.9	77.8 (~1)

Table 3. Values of density (g/cm^3) and crystallinity (%, bold) of gels and initial polymers

Number of freezing/thawing cycles	Gels		Initial polymers	
	PVA I	PVA II	PVA I	PVA II
1	1.278	1.265		
2	1.278	1.262	1.280	1.300
3	1.264	1.277	**54**	**58**
	43	**44**		

Density and crystallinity of gels

Density and crystallinity values of dry gels compared with initial polymers are presented in Table 3. The density values of gels (for three freezing/thawing cycles) are slightly less because of somewhat lower crystallinity.

CONCLUSIONS

– Satisfactory yield of PVA gel can be achieved for the content of PVA in water solution of about 15% by using the freezing/thawing method. A high content of separated sol fraction is recorded at lower concentrations of PVA (5% and 10%).
– Poly(vinyl alcohol) with a low value of molecular weight (25 000, 80 000) either poorly forms gel or does not form gel at all.
– The gel fraction of PVA with a higher molecular mass (130 000, 145 000) increases with the number of freezing/thawing cycles and reaches 80% and more. Yet, satisfactory values of gel fraction could be reached even at the first freezing/thawing cycle.
– The equilibrium value of water content, W_{eq}, in gels increases with the rise in the exposure temperature

and more feasibly due to the increase in the compliance of the cross-linked network.
– The equilibrium water content for repeated water absorption, W_{eq}^*, does not differ significantly from the respective W_{eq} values. This indicates that the cross-linked network structure of obtained gels is stable enough.

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Polüvinüülalkoholi hüdrogeelid

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Hüdrogeelid on valmistatud polüvinüülalkoholi alusel. On uuritud vee absorptsiooni, geeli fraktsiooni ja eri geelide tihedust, mis on valmistatud külmutamis-/sulatamismeetodil.